Irradiation-Modification of Starch-Containing Thermoplastic Blends. I. Modification of Properties and Microstructure

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SYNOPSIS

Irradiation-modification of the blends of various starches with a synthetic polymer [poly (ethylene-co-vinyl alcohol)] was carried out using an electron beam. The effect of irradiation on neat starches was studies using gel permeation chromatography. Changes in the thermal and mechanical properties of the blends, as well as in their microstructures, were also evaluated. The data indicate, consistent with other reports in literature, that starch molecules fragment under the effect of ionizing radiation, while the EVOH is relatively unaffected. These substantial (mainly physical) modifications to the starch molecules manifest themselves in changes in the thermal behavior of the blends. Furthermore, the mechanical properties of filaments obtained from molten irradiated pellets were quite different from those of control filaments, at least for some starches. Micrographic examination of some blends indicated a correspondence between a modification in the microstructure of the filaments and a change in their mechanical properties. It seems likely that the enhanced mobility of the fragmented starch molecules in the melt is responsible for these changes in the microstructure and concomitantly, the mechanical properties of the blend. Such an irradiation-based physical modification of starch may be of use in tailoring the properties of commercial blends of starches with synthetic thermoplastics. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The adverse environmental impacts of disposing solid wastes have become increasingly apparent in the last few decades. This, coupled with the projected sharp decline in landfill availability,[1],† has resulted in a greater emphasis being placed on issues relating to solid waste generation and disposal. Among the various materials that comprise solid wastes, polymers have been the focus of much attention for a number of reasons, a major one being their lack of

degradability upon disposal. Among the various strategies to ameliorate the problems related to plastic disposal, a promising one (at least for some specific applications) is the use of plastics that degrade in the natural environment.

There are a number of different approaches to achieving environmental degradability in thermoplastics.[2],[3] It is possible to introduce degradability into certain synthetic polymers through chemical modification routes, such as introducing linkages in the carbon backbone that make it susceptible to hydrolysis or photodegradation. Unfortunately, such chemistry-based approaches generally add complexity to the synthesis procedures, which can ultimately adversely affect the economics of production. A different approach, and one that has been receiving significant atten-

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† The United States Environmental Protection Agency has estimated that by the year 2006, the number of landfills in the United States is expected to decline by 80% of the 1986 levels.[1]

tion, is to use natural polymers either by themselves or as components of thermoplastic blends, using the fact that molecules of biological origin will eventually degrade in the environment under the action of microorganisms.

Starches, a class of natural polysaccharides produced by most plants as a method for storing energy, have been the specific focus of much attention due to an abundance of feedstocks from agricultural crop sources in the United States, even though these biopolymers do not exhibit physicochemical properties that allow them to be used by themselves (at least in an unmodified form) as commodity thermoplastics. For this reason, although a number of different approaches have been attempted to utilize starch commercially for biodegradable plastics applications, almost all have involved compounding starches in some form with synthetic thermoplastics. The most common (and one of the simplest) of these involves the compounding of native, unmodified starch with autooxidant-containing polyethylene, whereby the starch acts as a granular filler and serves to enhance the free-radical-based degradation of the synthetic polymer.[4-6] Another route that has been explored is the blending of gelatinized, modified, or plasticized starch with synthetic polymers such as poly(vinyl chloride),[7] as well as poly(ethylene-co-acrylic acid) and polyethylene.[7-10] Some subsequent research efforts have explored newer formulations consisting of blends of starch with other synthetic polymers such as poly(caprolactone),[11] or natural polymers such as poly(hydroxy alkanoates).[12]

One common feature of all these various processes is that the starch does not really melt under these conditions of compounding (since the melting point of native starch is higher than the blending temperatures). The fact that high concentrations of plasticizers can significantly depress the melting and glass transition point of starch under high pressure and allow it to be processed like a thermoplastic has been the basis of newer processing procedures developed in the last few years.[13,14] Unfortunately, even though pure starch can be melt-processed under these specific conditions, it is still unusable by itself for most end applications because of its generally unsatisfactory mechanical properties and their dependence upon the starch water content (the latter in turn can vary greatly with the ambient conditions). Consequently, successful commercial use of thermoplastically processed starch still requires blending with other degradable polymers that lend acceptable mechanical and physical properties to the blend. Examples of biodegradable synthetic polymers that have been explored in the past and re-

cently for blending with starch include poly (vinyl alcohol)[15,16] and poly(ethylene-co-vinyl alcohol).[17]

Although the blending of starch with thermoplastic materials has been attempted in various forms mentioned here over the last two decades, it is only recently that the interrelationships between the processing parameters, the morphology, and the properties of such blends are beginning to be studied in a systematic manner (e.g., Simmons et al.[18]). Generally, it is seen that the addition of starch to thermoplastics has adverse effects on the mechanical properties, as is evident from a lowering of the ultimate tensile strain and stress values for these blends as compared to the neat thermoplastics (e.g., Ramsay et al.[12]). Some reports in the literature indicate that the physical and mechanical properties of starch-containing plastics can be favorably modified by derivatization of the starch previous to the blending. This has included modification of the surface of the starch granules,[19] as well as at the molecular level.[20] Such an improvement of properties is presumably due to changes in the interactions between the (derivatized) starch and the thermoplastic with which it is blended, and hence changes in the morphology of the blend. However, the mechanisms underlying these property modifications do not seem to be completely clear, especially since the morphology of starch-containing blends has generally been studied only to a limited extent by techniques such as scanning electron microscopy, and recently by transmission electron microscopy.[21] Still, these observations highlight the importance of studying the interactions at the molecular level between the starch and the blending thermoplastic, their relationship to the processing and the structure of these blends, and the implications therein for the physical-mechanical properties of such composites.

The aim of the current work was to study the effect of molecular modification of starches on their blends with thermoplastics. In contrast to most of the previous studies reported in literature, our objective was to attempt to impart significant structural modifications to the starch molecules without significantly altering its chemical structure. In the present study, starch modification was carried out by means of electron-beam irradiation of a series of precompounded blends of starch and poly(ethylene-co-vinyl alcohol). Following this, the thermal and mechanical properties of these blends were studied over a range of starch-synthetic polymer compositions for different kinds of starches. Brief studies were also carried out on the morphology and other physical characteristics of these blends in order to understand the relationships between the radiation

**Table I Compositions and Processing Parameters for the Main Series
of Starch/EVOH Blends (from George et al.[17])**

Nomenclature	Starch (wt %)	Feed Weight Fraction (Solids)	Feed Weight Fraction (Glycerin)	Feed Weight Fraction (Water)	Extruder RPM	Extruder Peak Temperature (°C)	Output Flow Rate (kg/h)
Waxy Maize							
WM 100	100	0.750	0.150	0.100	131	190	11.4
WM 70	70	0.773	0.150	0.076	114	190	17.3
WM 50	50	0.732	0.138	0.130	115	190	19.2
WM 30	30	0.727	0.135	0.138	129	190	17.7
Native Corn							
NC 100	100	0.671	0.134	0.195	160	119	14.2
NC 70	70	0.698	0.136	0.166	120	194	19.8
NC 50	50	0.706	0.133	0.161	125	190	19.2
NC 30	30	0.735	0.136	0.129	137	190	18.3
Hylon VII							
HY 100	100	0.686	0.137	0.177	150	170	13.4
HY 70	70	0.659	0.129	0.212	130	190	18.0
HY 50	50	0.651	0.126	0.224	149	190	19.8
HY 30	30	0.702	0.129	0.169	125	190	18.7

modification of these blend materials and its effect on their subsequent processing, morphology, and mechanical properties.

EXPERIMENTAL

Three different kinds of corn starch (National Starch Co.) were utilized in this study, differing essentially in their relative fractions of amylose and amylopectin as follows: a waxy maize starch (Amioca), essentially 100% amylopectin; a native corn starch (Melojel), approximately 70% amylopectin and 30% amylose; and a physically modified high-amylose starch (EK Fl. Hylon VII), approximately 30% amylopectin and 70% amylose. These are subsequently referred to as WM, NC, and HY, respectively. The other major component of the blends, the synthetic polymer, was a random copolymer of ethylene and vinyl alcohol, namely poly(ethylene-co-vinyl alcohol) (Eval Corp., EVAL E105A), 44 mol % ethylene, and number- and weight-average molecular weights of about 50,000 and 100,000, respectively, referred to as EVOH in this paper.

Blend Preparation

The compounding of the blends was carried out using a 34 mm co-rotating twin-screw extruder (Leistriz) at the Novon Division of the Warner Lambert Corporation. The dry feed to the extruder consisted of a mixture of starch powder and EVOH pellets (conditioned at 50% relative humidity) along with a small quantity (<1%) of naturally occurring emulsifiers, such as glycerides, lipids, and fatty acids to serve as processing aids. For each of the starches, a series of blends were prepared by varying the relative proportions of the starch and the EVOH in the dry feed. Glycerin (approximately 15% by weight of the dry feed) and some additional water were added to the extruder through liquid ports. The total amount of plasticizer (glycerin and water) inside the extruder varied from 23% to 35%, with average values of 25%, 30%, and 33% for the blends containing waxy maize, native corn, and high-amylose starch, respectively. The total output flow rate (from a mass balance of the system) was calculated to be approximately 11–14 kg/h for the neat starches and 20 kg/h for the blends. The extruder speed during the blending was between 110 and 160 rpm for all the blends, and the maximum temperature was about 190°C (except for the neat native corn and high-amylose starch, where the temperature had to be lowered). Table I lists the main series of blends used in this study, their processing parameters, and feed and output rates. As can be seen there, these blends consisted of 30%, 50%, and 70% starch and the rest of EVOH (on a dry basis). A second series of blends prepared subsequently (with 15%, 40%, 60%, and 85% starch) was also utilized for some of the mechanical testing; but for the sake of brevity, their composition and processing details for this series are not presented here.

Table II   Water and Glycerin Contents of the Main Series of Starch/EVOH Blends as Compounded and As Conditioned (from Villar et al.[22])

Blend	Glycerin Content (As Compounded)	Water Content (As Compounded)	Water Content (As Conditioned)
WM 100	16.1	7.8	9.5
WM 70	16.3	5.3	8.3
WM 50	14.8	9.0	7.1
WM 30	12.7	7.5	6.0
NC 100	12.2	15.8	9.8
NC 70	18.1	12.7	8.5
NC 50	16.1	9.9	6.9
NC 30	13.6	6.8	5.9
HY 100	15.1	8.7	8.1
HY 70	14.8	10.6	7.9
HY 50	15.6	12.1	7.5
HY 30	14.1	8.0	5.9
EVOH	14.1	0.3	6.9

Irradiation of Blends

The electron-beam irradiation treatment of the blends was carried out at the Massachusetts Institute of Technology High Voltage Research Facility, utilizing a compressed-gas-insulated Van de Graaff Electron Accelerator, with an electron-beam energy of about 2.5 MeV, and a dose rate of about 2500 Grays s^{-1}. The samples were placed in sealed polyethylene bags prior to the irradiation (this step was carried out on the lab bench; therefore, the pellets were in an air environment) and placed on a moving belt under the beam exit. Since the depth of penetration of the electrons is limited to a few millimeters, care was taken to maintain the sample thickness below approximately 5 mm. The total dose delivered was determined by the belt speed and the number of passes under the beam. The blend pellets were irradiated, as were the samples of filaments prepared from control pellets, at room temperature. The overall dose delivered was in the range of 10–200 kGys (1 to 20 megarad).

The equilibrium water content of the blends depends upon the ambient conditions due to the hydrophilic nature of starch. Since water molecules can have a significant interaction with the radiation, variations in the blend moisture content could lead to variation in the effect that the irradiation would have on the blends. The water content can also influence the properties of starches (and hence the blends). For this reason, all the materials were conditioned under fixed conditions for at least one week to regulate the moisture content before each of the experimental steps. This was achieved by placing them in a closed chamber at room temperature (23°C) and 65% relative humidity. Therefore, the blends were conditioned before and after the irradiation treatment, as well as after the preparation of samples from irradiated pellets. Table II lists the glycerin and moisture contents as compounded (for the main series of blends), and also the moisture content after conditioning.[22]

Chromatography of Irradiated Starches

The experiments were carried out on the DAWN-F (Wyatt Technologies) multiangle laser light scattering (MALLS) detector ($\lambda = 6328$ Å) coupled to a 150-C Gel Permeation Chromatography system (Waters Corp.) using Toyo Soda 4000PWXL and 6000PWXL columns connected sequentially with a guard column, with the temperature of the column compartment at 28°C. The mobile phase was aqueous $0.5N$ NaOH with a flow rate of 0.46 mL/min. The samples for the chromatography were prepared by dissolving them under nitrogen in degassed $0.5N$ NaOH and subsequently filtering with a Millipore LCR 0.5 μm filter prior to injection. The experiments were performed on the control and irradiated WM 100, NC 100, and HY 100 samples. Dextran standards (Fluka Chemical Co.) were used for calibrating the differential refractometric detector (DRI) detector response. For the experimental samples, the concentration of starch in an elution slice was then obtained from its DRI response. The

values of the differential refractive index increment (dn/dc) used in the calculations were as follows: 0.146 for the starches and 0.142 for dextran.[23] The GPC-LS calculation were performed using the Astra 2.11B software (Wyatt Technology). The interdetector lag for this experiment was estimated to be 0.28 mls and was obtained by matching the DRI and 90° light scattering signals from an injection of bovine serum albumin (BSA), a monodisperse protein.

Thermal Analysis

The calorimetric studies were carried out only on 50/50 blends irradiated at 200 kGys; but in this case, the irradiated pellets, the filaments obtained from these pellets, and the respective controls were studied. A differential scanning calorimeter (Perkin Elmer DSC 7) was utilized for this study. The samples were placed in pressure-tight stainless steel pans (which were preferable for these blends due to the presence of a large amount of volatiles) and were heated at a rate of 10°C/min from 25 to 190°C. At the end of the run, the sample was cooled at a rate of 10°C/min until the temperature of the sample was brought down to 25°C, at which point the second heating run was initiated (with the same parameters as the first heat).

Mechanical Testing

For the tensile testing, filaments were prepared from the control pellets as well as the irradiated pellets by using a capillary rheometer. For all the samples, the processing through the rheometer was carried out at the same conditions, namely, at a temperature of 150°C and a plunger velocity of 5 mm/min (corresponding to a nominal shear rate of 133 s^{-1} and a corrected shear rate of 150–200 s^{-1}, depending upon the sample). The mechanical testing on the conditioned filaments was carried out on an Instron Model 4505 Universal Testing Machine.

Although pneumatic grips were used to hold the filaments during the tensile testing, smooth or serrated grip surfaces were found to be unsuitable. The smooth jaws had trouble providing enough friction to hold the filaments tightly, whereas serrations on the jaw surfaces tended to serve as areas of stress concentration leading to failure at the grip. A reasonable solution was to deposit a thin cross-linked rubber coating on the gripping surface of the smooth metal jaws. This coating allowed the samples to be held firmly without causing local necking. With such grips, since the samples are held over a finite length, the effective gauge length can be higher than the

actual separation between them, which can affect the absolute values of the initial tensile modulus (as can the compliance of the rubber coating itself). However, since we were mainly interested in estimating the relative property changes for the irradiation-modified samples in comparison to the controls, these grips still serve our purpose as long as the same ones were used for the experimental and control samples with the assumption that the effective gauge length should not vary significantly from sample to sample. Also, due to the effective gripping point being slightly inside the grip, the filaments were sometimes drawn inside the grip at higher extensions. The strain-to-break values were corrected to account for this slip. It was not possible, however, to correct the values of the modulus since it was difficult to estimate the relative contributions of these various effects at very low strains; therefore, these values are not presented here.

At least ten filaments were tested for each blend. The nominal gauge length was 25.4 mm, and the extension rate was 60.96 mm/min, as per ASTM D 3822-91.[24] The data were collected using the Instron mechanical testing program and reanalyzed using a graphics package (Grapher) to correct for the initial effects at the beginning of the test. Three sets of samples were studied: the control filaments, filaments prepared from 200 kGys irradiated blend pellets, and 200 kGys irradiated filaments prepared from the control pellets. These samples were studied for a composition range varying from pure EVOH to 70% starch–30% EVOH for each of the three kinds of starches. The effect of the radiation dose for the WM 50, NC 50, and HY 50 filaments was also briefly studied.

Morphological Studies

For the morphology studies of the blends, we chose to study only the filaments that were prepared from 50/50 blend pellets that had received a radiation dose of 200 kGys, since these showed some of the most significant changes in the mechanical properties. The experimental and control filaments were freeze-fractured under liquid nitrogen and then suspended in an amylase-amyloglucosidase solution (approximately 10 units α-amylase, 3 units β-amylase, and 25 units amyloglucosidase per mL of a 200 mmol sodium acetate buffered solution, with pH 5.0) for 2 h at 37°C. The filaments were then rinsed with water, air-dried overnight, and then examined under an environmental scanning electron microscope (ESEM) (ElectroScan Corp.). Irradiation of starch seemed to increase its susceptibility to beam

damage under regular SEM conditions; therefore, the milder examination conditions (lower beam energy and higher chamber pressures) offered by the ESEM were preferred.

RESULTS AND DISCUSSION

The effects of radiation on a polymer in the solid state are a function of a variety of factors such as the type, energy, and dose of radiation, as well as the physical and chemical characteristics of the particular polymer. Radiation with sufficient energy to cause ionization (such as fast electrons or gamma rays) can cause significant changes in polymers at the molecular level through the formation of ions and radicals that are, in turn, responsible for chain scission, cross-linking, and other reactions.[25] At a given temperature, the interaction of such radiation with the polymer molecules is determined to a large extent by the chemical composition of the polymer and the environment of the molecules. Even for a fixed chemical composition, factors such as the morphology of the solid polymer and its molecular mobility can play a role in determining the final outcome of the radiation effects. For example, from studies on irradiation of cross-linkable semicrystalline polymers such as polyethylene, it has been inferred that although radiation effects generally predominate in the amorphous regions of the polymer, they eventually have a strong impact on the melting and crystallization behavior of the overall sample. Furthermore, if the irradiation is carried out in air, the oxidative reactions (during and subsequent to the irradiation) between the radiation-generated radicals and the oxygen present in the sample can also be significant.

Most studies on the radiation effects on synthetic polymers have focused on polyethylene because of both its simple molecular structure and its commercial importance. There has been only limited exploration of the effects of radiation on other polymers in the solid state and very little work on the irradiation on EVOH. The formation and decay of alcohol, alkyl, and polyenyl radicals in EVOH irradiated in air and in vacuo have been studied using electron spin resonance.[26] The alcohol radical decay (in air and in vacuo) followed second-order kinetics, indicating a mutual coupling reaction, while the polyenyl radicals decayed in air according to first-order kinetics, attributable to reaction with oxygen molecules that diffused into the solid polymer. Reactions between alkyl radicals and oxygen were also shown to result in the production of moieties such

as carbonyl, although these radicals also seemed to lead to the formation of cross-links. Though this work indicated that the irradiation of EVOH results in the production of some cross-links and other products of radical-based reactions, overall, the data on oxygen transmission and mechanical properties seem to indicate the relative insensitivity of EVOH to irradiation, at least in the dose ranges relevant to our experiments. Other work on the radiation-induced oxidative degradation of EVOH indicates that peroxyl radicals could be responsible for some scission at the sec-alcohol sites;[27] although in the case of EVOH, one would expect the oxygen effects to be lower than those traditionally seen for polymers such as polyethylene, since the solubility of oxygen in EVOH is quite low. Ekman and Nasman[28] have also indicated that electron-beam irradiation of EVOH does not lead to gel formation in the polymer. These observations are consistent with our own studies on the melt-rheology of EVOH.[29] Overall, the behavior of irradiated EVOH seems to fall between that of polyethylene (mainly cross-linking) and poly vinyl alcohol (mainly scission).

For starches, it has been shown that ionizing radiation can result in significant physical modification,[30] resulting in molecular weight reduction through chain scission (as evinced from intrinsic viscosity measurements[31]), as well as a reduction of the strong intermolecular forces that are often present in native starches (indicated, for example, by an increase in their dispersibility upon irradiation[32]). For starches (and other hydrophilic polymers), the amount of water can vary significantly depending upon the ambient conditions. This can be an important variable in a radiation experiment; for example, for solid starches exposed to ionizing irradiation, water can have a "protective effect"[33] and the radiolysis products of water often participate in reactions with the macromolecules.[34] The process of irradiation can also result in some chemical changes in the starch polymers with introduction of functional groups such as carbonyl and carboxyl moieties.[35] These changes in starch at the intermolecular and intramolecular level are likely to affect its processing as well as the eventual morphology (and the properties) of the its blends with other materials.

Chromatography of Irradiated Starches

Figure 1 presents the DRI detector trace versus elution volume for the three different starches (control and irradiated samples). It should be kept in mind here that the magnitude of the DRI signal is pro-
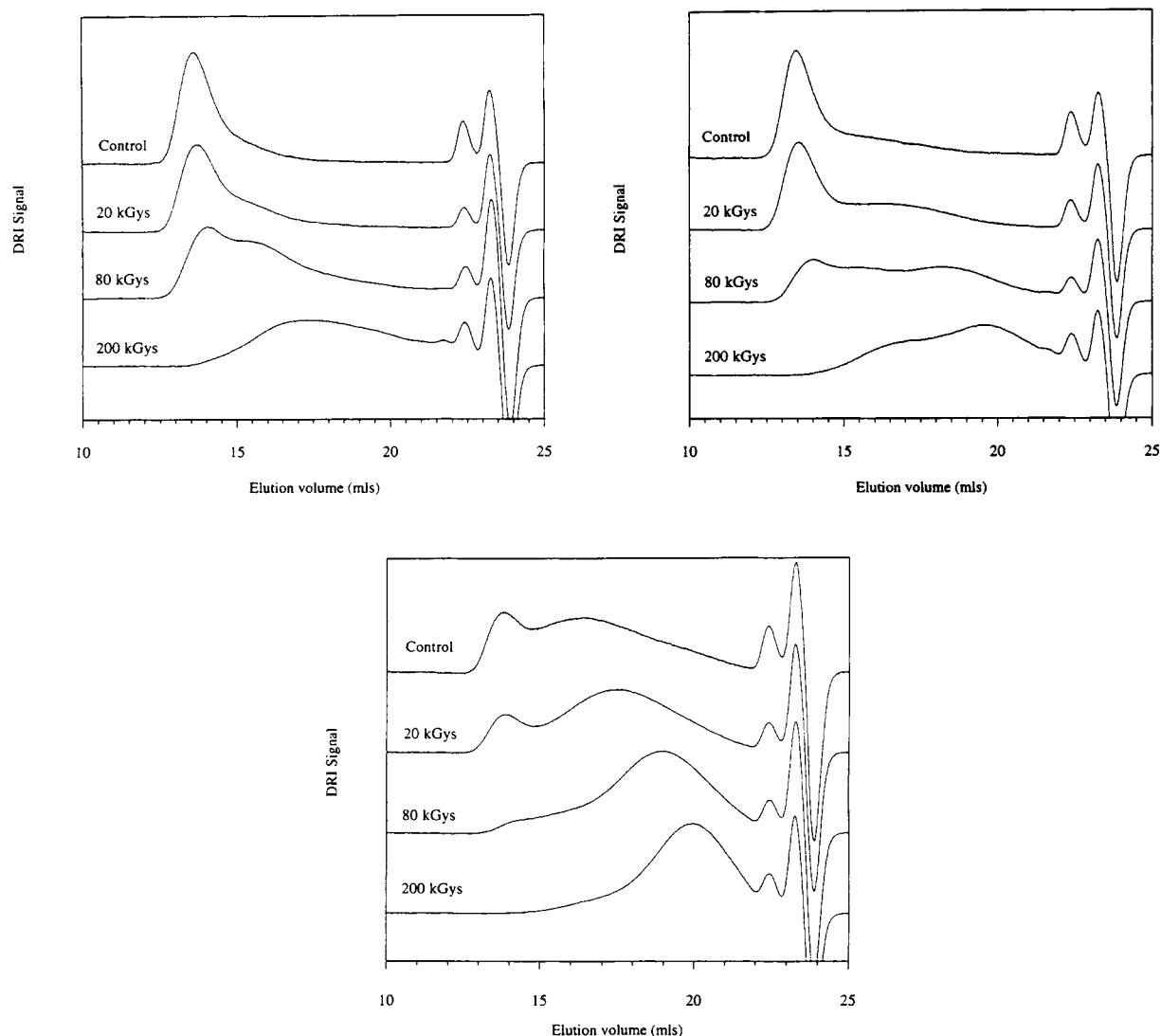
Figure 1 DRI detector traces from chromatography of control and irradiated starches: (a) WM 100, (b) NC 100, and (c) HY 100.

portional to the concentration of the macromolecules in any elution slice. As these data indicate clearly, increasing radiation doses results in an increase in the elution volume of the macromolecules. In a GPC experiment, the hydrodynamic size of a molecule determines its time of elution from the columns. Larger molecules have access to a limited number of pores in the packing and elute early, while smaller molecules can access a much larger number of pores resulting in longer elution times. Therefore, a shift of the curve to higher elution volumes upon irradiation is consistent with the model of ionizing-radiation-induced chain scission in the starch macromolecules.

Some subtle differences between the response of the different starches to ionizing radiation can be

seen. Figure 1(a) shows the DRI trace for the control and irradiated waxy maize samples. It is seen that the control sample has a peak with a sharp initial rise at an elution volume of about 13.5 mLs. This elution volume represents the exclusion volume for this column set (theoretically corresponding to poly(ethylene oxide) of molecular weight $\approx 10^7$ daltons), indicating that the control WM 100 sample consists of (a sizable fraction of) very large molecules that are excluded from the pores of the column (not surprising, given that amylopectin molecules have molecular weights exceeding 10^7 daltons and often even greater than 10^8 daltons[36]). Upon irradiation, the peak broadens and shifts to higher elution volumes but stays unimodal in character. This is consistent with the fact that the waxy maize starch
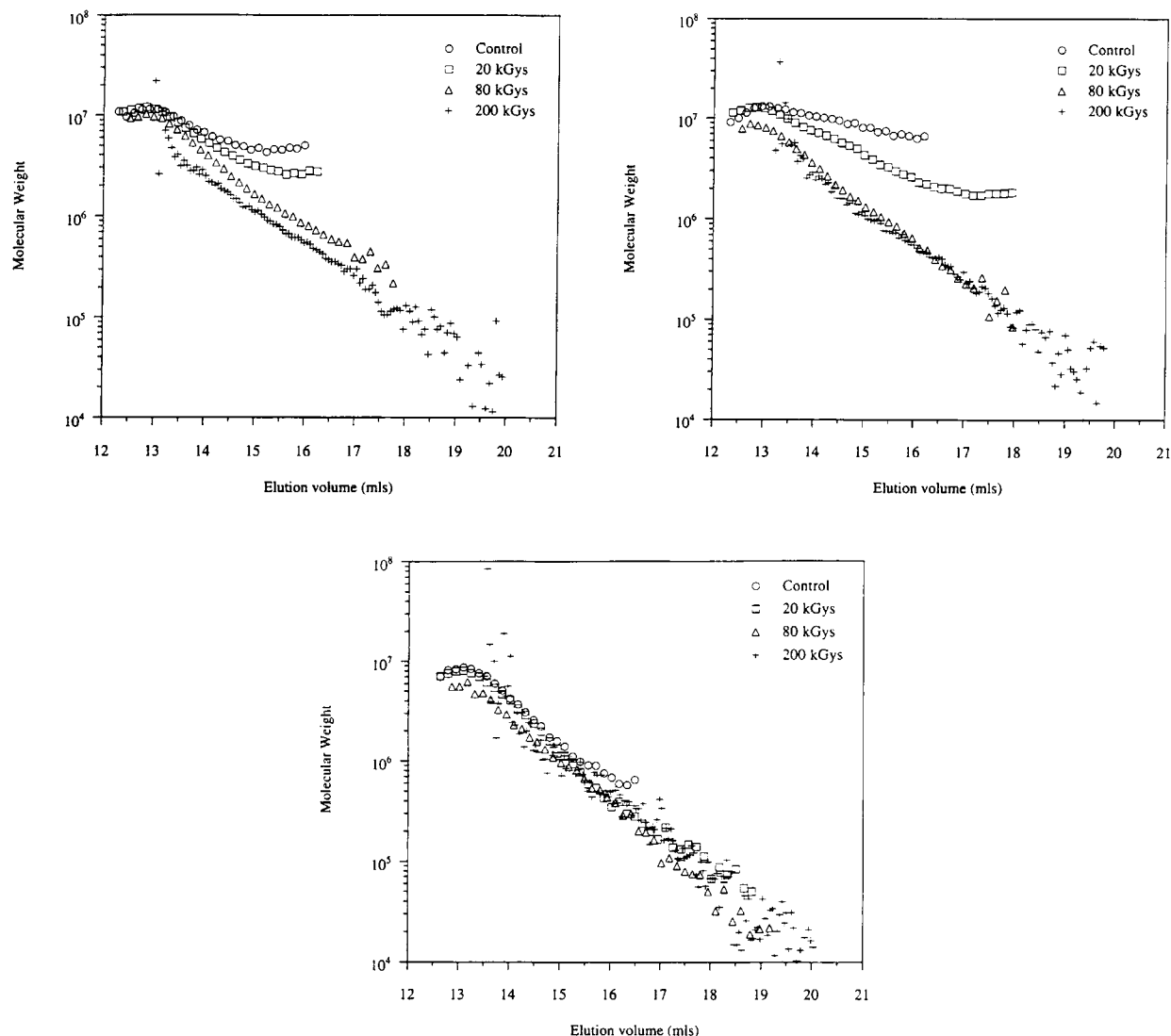
Figure 2 Molecular weight as a function of elution volume for control and irradiated starches: (a) WM 100, (b) NC 100, and (c) HY 100.

contains only one species of molecules, i.e., amylopectin. Figure 1(b) shows the DRI response of the native corn samples. In this case also, the control sample has a steep rise at the exclusion volume of the column set, although the peak has a slight tail. This is probably due to the amylose fraction present in this variety of starch. Upon irradiation, the large initial peak diminishes in size, with the appearance of a broad peak at higher elution volumes. At higher irradiation doses, the overall curve continued to display a somewhat bimodal character. The high-amylose starch data is somewhat similar [Fig. 1(c)]: the control sample displays a bimodal peak, presumably due to the amylopectin and the (dominant) amylose component. For the irradiated samples, the amylopectin peak slowly reduces in size, while the

second peak shifts to higher elution volumes and becomes more prominent with increasing radiation dose. In fact, for the 200 kGys irradiated HY 100, only one peak is observable; it is also noticeable that this peak is not as broad as the 200 kGys irradiated samples from the other two starches.

Figure 2 shows the molecular weight versus elution volume plots for these samples as obtained from the light scattering and the DRI traces. It should be mentioned that the calculations that led to these plots are quite approximate since the same value of the dn/dc is used for the irradiated samples as for the controls. (The actual value of the dn/dc is expected to change somewhat since irradiation of starch in air is known to result in the introduction of some functional groups on the glucosidic repeat

Table III   DSC Data (Second Heat) for Control and 200 kGys Irradiated EVOH and 50/50 Blend Pellets

Sample	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g_{sample})	ΔH (J/g_{EVOH})
EVOH (control)	124.0	140.1	39.26	49.73
EVOH (200 kGys)	122.0	139.6	39.39	49.90
WM 50 (control)	128.7	137.4	18.06	46.25
WM 50 (200 kGys)	117.9	129.2	19.41	49.70
NC 50 (control)	136.0	144.0	17.36	45.09
NC 50 (200 kGys)	114.4	125.9	16.21	42.10
HY 50 (control)	123.7	135.8	14.31	37.22
HY 50 (200 kGys)	106.2	120.3	14.32	37.24

units.) In any case, these calculations still serve our purpose since we are interested more in the general changes in the molecular weights of the starches rather than their absolute values.

Some interesting general trends can be seen here. The data for the lowest elution volumes for all the control samples indicate that the molecular weight is almost constant; these elution volumes contain the molecules that were excluded from the columns and therefore do not display any chromatographic separation. Furthermore, data for waxy maize and native corn also indicate that the molecular weight versus elution volume plot is relatively flat. This is somewhat surprising since such a behavior is indicative of molecules that have a range of hydrodynamic sizes for similar molecular weight. Studies with highly branched molecules such as star molecules have indicated that (for a given branch length) the hydrodynamic volume does not change much with molecular weight.[37,38] The kind of behavior seen in our case would happen only if these samples have a mixture of molecular species of almost unchanging molecular weights where molecules with a lower degree of branching have longer branches (thus allowing the hydrodynamic volume to change while the molecular weight does not change much). Although this is theoretically possible, it does not seem very likely that this is the case. It seems more likely that the separation mechanism operating on these starch molecules may differ from the one assumed for a GPC experiment; thus, the separation may not be based exclusively on hydrodynamic size (which may not be surprising, again given the large sizes of these molecules). In any case, we see that for all the starches, irradiation leads to the appearance of a molecular weight versus elution plots that resemble traditional chromatographic data where there is marked drop in molecular weights with increasing elution volumes. It can also be seen that for any

given elution volume, starches exposed to higher radiation doses generally have lower molecular weights. Since molecules with less dense branching possess a lower molecular weight for a fixed hydrodynamic volume, it seems that the starches with higher radiation doses are less branched than the control or lightly irradiated starches. Furthermore, for all the three starches irradiated with 200 kGys, the plots are quite similar: i.e., the radiation-based fragmentation renders the samples' chromatographic behavior similar, regardless of their initial differences.

Thermal Behavior

Data from the DSC studies on the control and irradiated EVOH and 50/50 blend pellets are shown in Table III. (Only data for the second heat are tabulated here.) The DSC scans on the control and irradiated EVOH pellets do not yield any notable change in the shape, size, or temperature of the endotherm, indicating that irradiation does not result in significant modification to the EVOH, at least not enough to cause an observable change in the recrystallization behavior of the irradiated material. This is in contrast to the observations for polyethylene, where both the overall level of crystallinity and the peak melting temperature decrease for irradiated samples.[39,40] The melting and crystallization temperatures for the EVOH pellets used in this study were lower than those reported for pure EVOH,[41] but that is expected given the high level of the plasticizer content in the materials used here and possible starch–EVOH interactions.

The endotherm in the 50/50 blend control pellets (HY 50, NC 50, and WM 50) corresponds to the melting of the EVOH crystallites. There are some differences among the blends in the peak temperature of the endotherm, as well as in the heat of fusion

per unit mass of EVOH in the sample. The WM 50 and HY 50 pellets display a endotherm peak at temperatures slightly lower than that of the (glycerin-containing) EVOH, but the NC 50 blend has a melting point slightly higher than that of the (glycerin-containing) EVOH. The area under the endotherm peak (corresponding to the crystallizable fraction in the EVOH) reduces as the amylose content of the starch used in the blend is increased. This could be attributable to the linear amylose molecules hindering the crystallization of the EVOH. During disruption of the starch granules, amylose molecules leach out before the amylopectin; therefore, during the extrusion, as the starch granules lose structure, it is possible that the starches containing higher amylose fractions could be responsible for a greater amount of relatively free amylose molecules interacting with the EVOH.

Examination of the irradiated blend pellets shows that endotherms occur at significantly lower temperatures in comparison to their control counterparts, although the area under the peak is essentially constant. Since for the EVOH pellets no drop in the melting temperature was seen, it is possible that in these blends the low molecular weight degradation products of the starches could be acting as additional plasticizers for the EVOH, thus lowering its melting point.
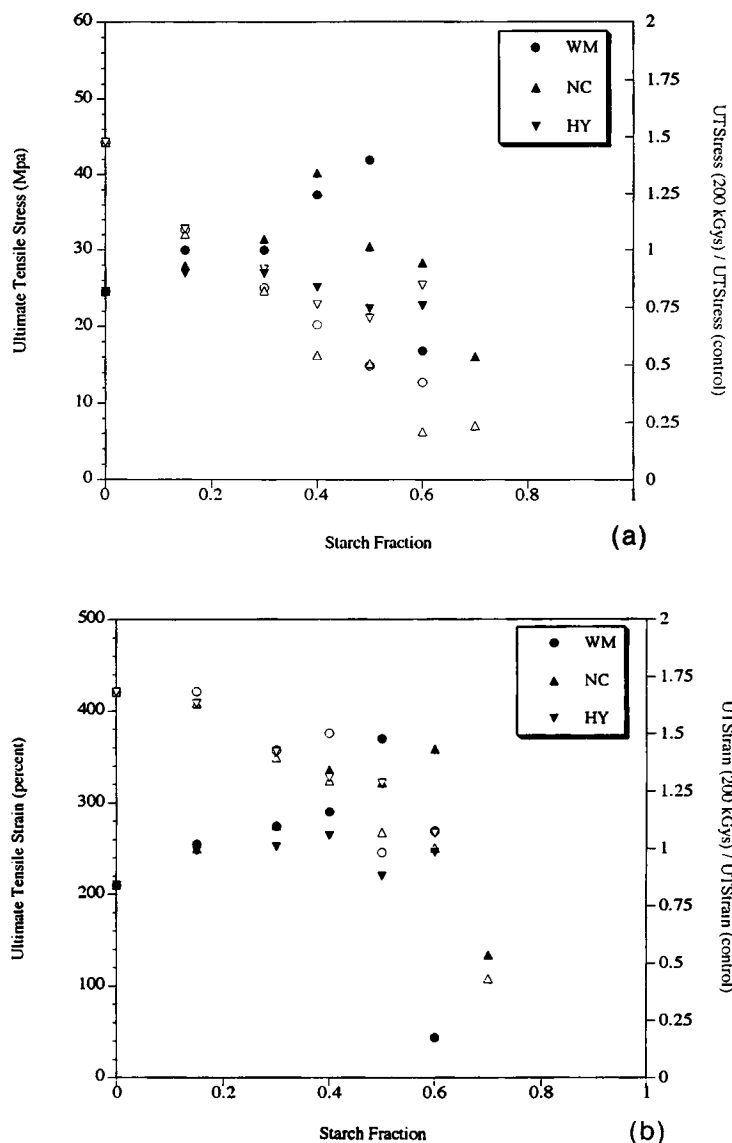
Mechanical Properties

Figure 3 shows representative nominal tensile stress versus strain curves for the EVOH and the 50/50 starch blends irradiated 200 kGys. Figure 4 shows the changes in the nominal ultimate tensile stress and the ultimate tensile strain of starch/EVOH blends upon 200 kGys irradiation, as compared to values for the control blends. Figure 5 shows changes in the same parameters (once again relative to the control materials) for 50/50 blends for a dose of 80 and 200 kGys. For these sets of data, the tests on irradiated materials were on filaments prepared from irradiated pellets (referred to as FIP). Figure 6 shows the changes in the same three parameters (between irradiated and control samples), except the irradiated samples here are filaments that were irradiated after preparation from unirradiated pellets (referred to as IF). Figure 6 shows representative nominal tensile stress versus strain curves for the EVOH and the 50/50 starch blends irradiated 200 kGys.

The mechanical properties of the irradiated EVOH did not show major changes as compared to the control samples (Figs. 4, 6), consistent with the rheological behavior for these blends reported else-

where.[29] The stress-to-break and strain-to-break values for both the sets of filaments show almost no change for the 20 kGys dose but then drop consistently (but only marginally) with increasing radiation dose. This trend also correlates well with the rheological behavior of the irradiated EVOH,[29] indicating that at the higher doses, some cross-linking occurs in the EVOH, which could manifest itself in lower ultimate tensile extension. These observations are also consistent with the work of Hama and Hirade,[26] i.e., overall the properties of EVOH are not modified significantly in the range of doses relevant to our experiments, although some cross-linking does occur at the higher doses. Interestingly, even though the trends for the two sets of filaments are similar, the overall magnitudes of the changes are different, with the filaments from irradiated pellets displaying higher stress-to-break and strain-to-break values. The cross-linking present in the EVOH is likely to be primarily in the amorphous part. Subsequent melting and resolidification of these pellets (as is the case for the filaments from irradiated pellets) would actually hinder recrystallization somewhat, therefore leading to smaller crystalline fractions in the material. The stress-to-break strain-to-break values depend more upon the amorphous fraction in a semicrystalline polymer.[42]

The mechanical properties of the FIP samples prepared from blends of starch and EVOH, however, show some significant changes as a consequence of irradiation (Fig. 4). For the samples containing 70% starch or more, the mechanical properties deteriorated greatly with 200 kGys radiation dose; in fact, it was not possible to obtain meaningful data from mechanical measurements on these samples. Such a sharp degradation in mechanical properties indicates that for these blends, the starch must be the dominant continuous phase on which the mechanical properties of the blends must be dependent, since starch is the only component of these blends that degrades significantly upon irradiation.

The same was not true of the blends with starch content of 50% or less. For these blends, it is noticeable that the trends for the FIP and IF samples are very different from each other (Figs. 4, 6). The properties of the blend IF samples change in a fashion somewhat similar to the EVOH IF samples, i.e., the stress-to-break and strain-to-break values decrease. However, the 200 kGys FIP samples show a very different behavior compared to the controls. The WM 50 and WM 30 filaments show an increase in the strain-to-break and stress-to-break values, with the effects being more pronounced for the WM 50. The NC 50 and NC 30 filaments show a trend
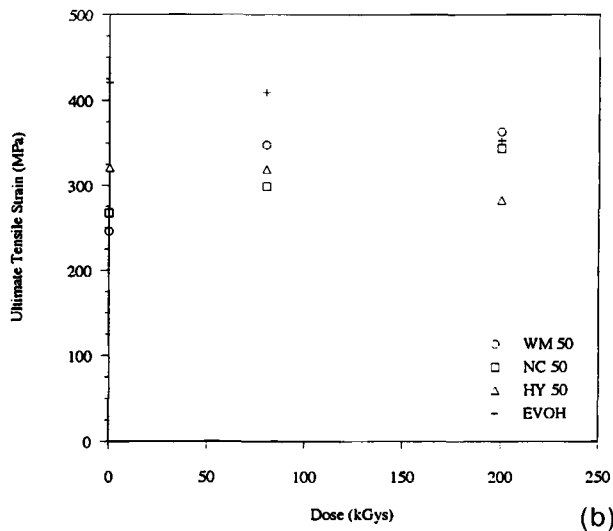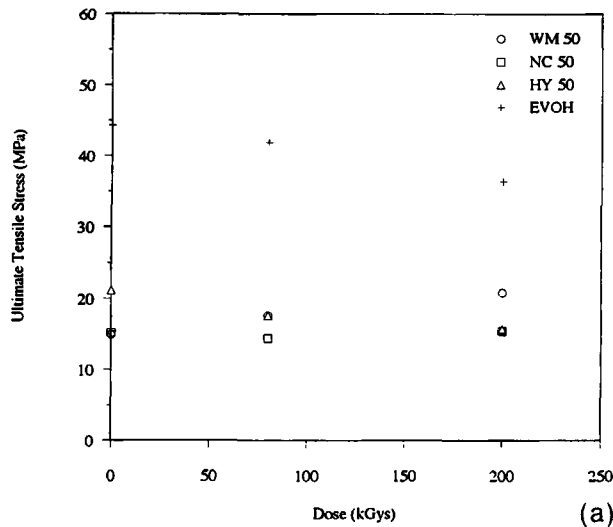
Figure 3   Mechanical properties of various control starch/EVOH blends (hollow symbols), and the changes in the mechanical properties of filaments from 200 kGys irradiated pellets (FIP) test samples for various blends relative to the corresponding control blend samples (filled symbols): (a) Nominal ultimate tensile stress and (b) nominal ultimate tensile strain.

similar to the waxy maize filaments, except that the magnitude of the differences between the control filaments and the samples prepared from irradiated pellets are not as high. The HY 50 and HY 30 filaments show small or no differences from the control filaments in the strain-to-break values, whereas the stress-to-break values decrease.

As an aside, it should also be mentioned that the diameters of filaments obtained from the starch/ EVOH blends were higher than that of the pure EVOH, though this might be due partly to some drawing of the EVOH filaments under their own

weight as they exited the capillary. More interestingly, it was also noticed that the diameter of the filaments produced from irradiated pellets are somewhat greater than those produced from the control pellets (for EVOH content of 50% or more), possibly indicating some general increase in the degree of die swell.
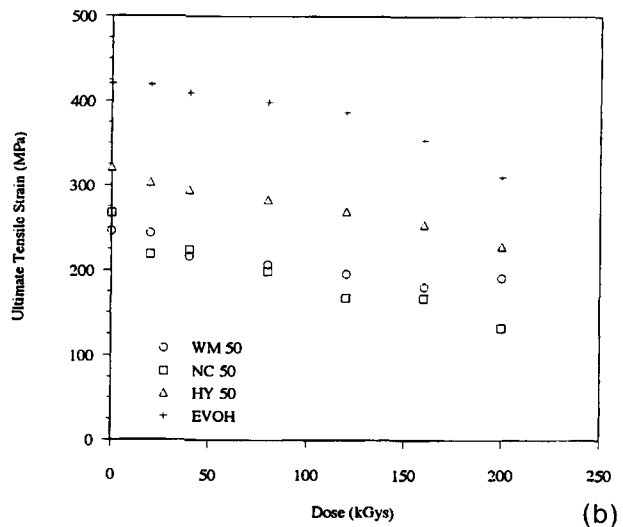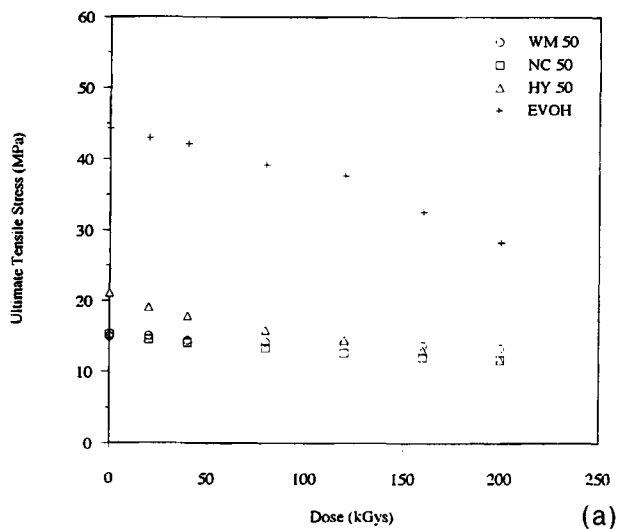
Irradiation studies on immiscible polymer blends have indicated that the individual components show the same response to radiation as the respective homopolymers. However, since the individual components of the blends can display very different re-

There have been a few experimental studies of the effect of ionizing radiation on the properties of polypropylene-containing blends. Upon irradiation, polypropylene was indicated to predominantly display chain scission[43,44] or a balance of cross-linking and chain scission.[42] (The second components of the different blends in these studies underwent cross-linking upon irradiation.) Furthermore, in all of these studies, irradiation was carried out on prepared samples with no further processing steps subsequent to the irradiation; i.e., the morphology remained fixed (similar to our irradiated filament samples). It was generally observed that with increasing radiation dose, while the tensile elastic modulus in-

Figure 4 Mechanical properties of irradiated filaments (IF) test samples for EVOH and 50/50 blends at different radiation doses: (a) Nominal ultimate tensile stress, and (b) nominal ultimate tensile strain.

sponses to radiation, the overall properties of the blends can be significantly modified by radiation (although it is often difficult to predict the overall consequences of the irradiation a priori). Much of the work on radiation modification of polymer blends has dealt with rubber modified thermoplastics, or compatibilized blends (where cross-linking of the rubber phase or formation of cross-links at the interface is mainly responsible for changes in the properties of the blends). These systems are very different from ours; therefore, it is difficult to relate our observations to the understanding gained from these other studies.

Figure 5 Mechanical properties of filaments from irradiated pellets (FIP) test samples for EVOH and 50/50 blends at different radiation doses: (a) Nominal ultimate tensile stress, and (b) nominal ultimate tensile strain.
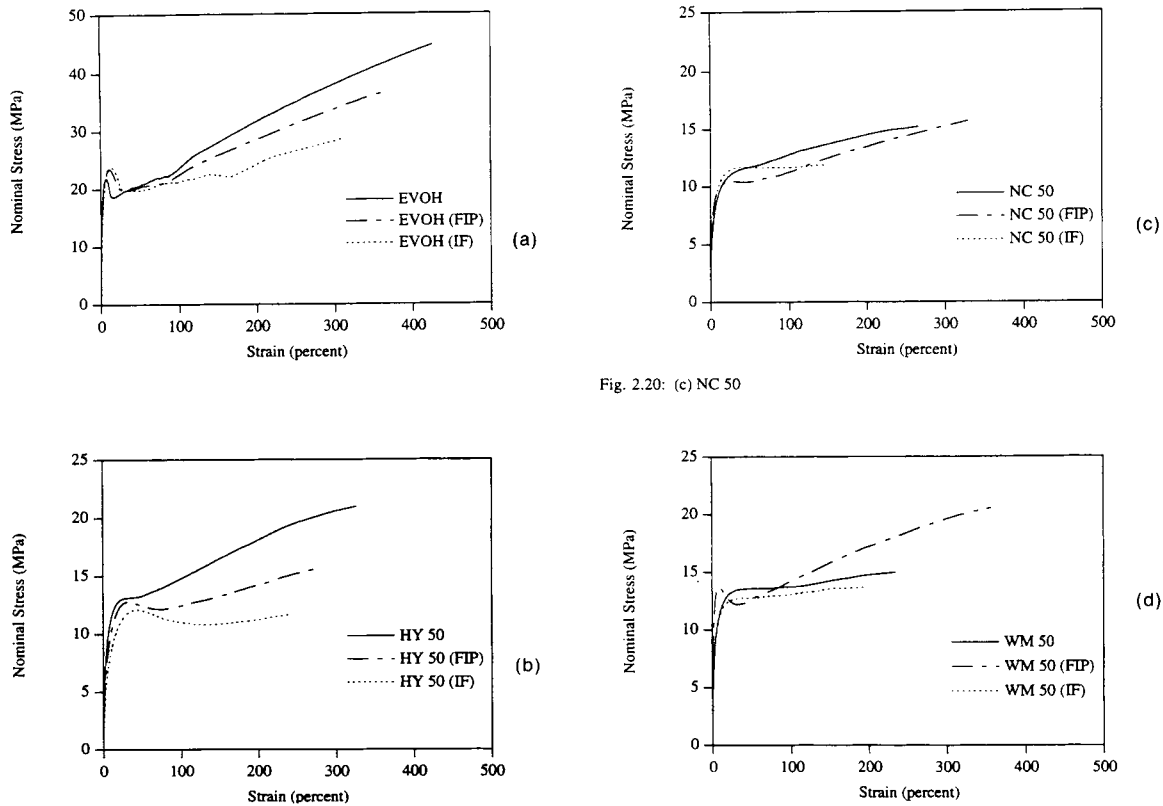
Fig. 2.20: (c) NC 50

Figure 6 Representative nominal stress versus nominal strain curves for control filaments, filaments from 200 kGys irradiated pellets (FIP), and 200 kGys irradiated filaments (IF): (a) EVOH, (b) HY 50, (c) NC 50, and (d) WM 50.
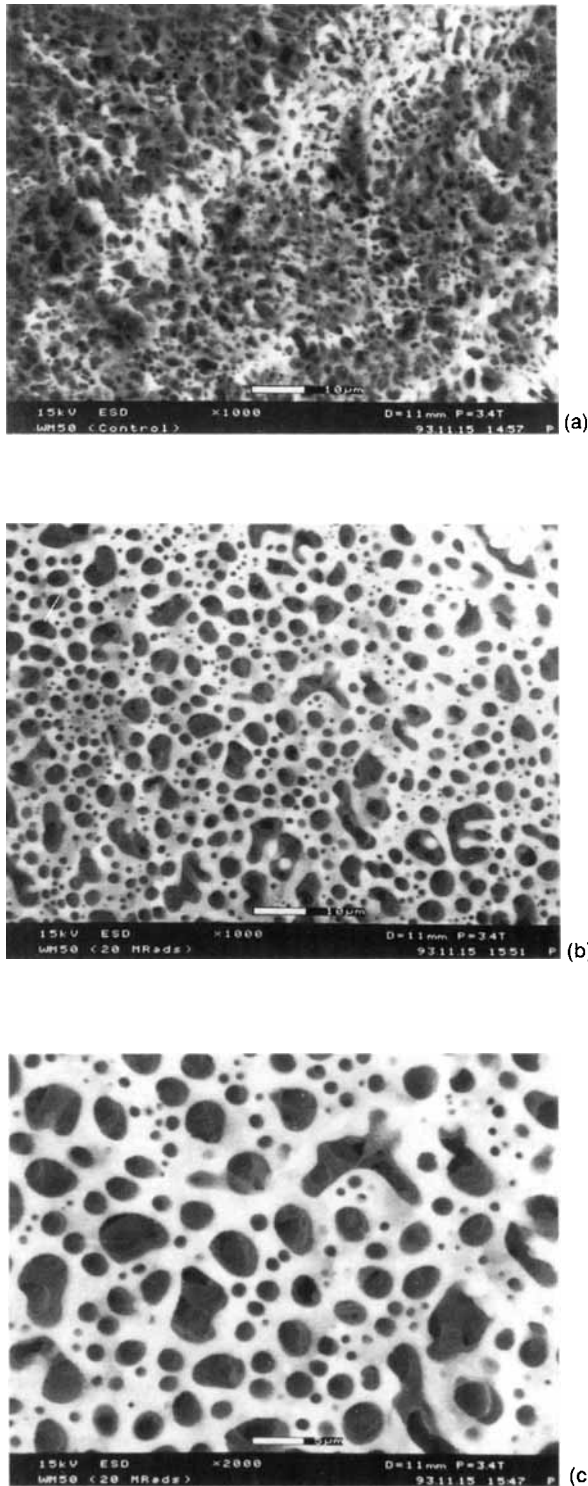
creased, the tensile strength dropped somewhat and elongation at break dropped quite significantly. Thomas et al.[43] noted that for their blends containing 70% poly(ethylene-vinyl acetate), the mechanical properties showed a remarkable difference in that the elongation at break increased dramatically upon irradiation. This was attributed to the continuous interpenetrating structure formed by this blend where, under the action of radiation, the cross-linking of the rubbery phase and the scission in the plastic phase led to a greater extensibility of the blend for reasons not completely explained by the authors. However, most of the general observation of these two studies are consistent with the a blend in which one phase displays cross-linking and the other chain scission upon irradiation (if the morphology remains fixed between the irradiation and testing steps). These results are similar to those for our IF samples. However, such a model cannot be simply applied to our FIP samples since the melt-processing subsequent to irradiation allows for changes in morhology as discussed in the next section. Huang[45] has indicated that gamma-irradiation of samples prepared from starch/EVOH blends can

influence their mechanical properties; but, once again, this experiment is similar to our studies on IF samples, since no melt-processing was carried out subsequent to the radiation treatment.

Morphology

The morphological studies on the filaments obtained from the 200 kGys irradiated 50/50 blend pellets, and the respective control filaments indicate some interesting changes upon irradiation. In the ESEM micrographs shown in Figures 7-9, there are two kinds of pictures: surfaces of the filaments, and the enzymatically etched cross sections of the filaments. For the latter kinds of micrographs, dark cavities represent the areas that initially contained starch (which was subsequently removed by the enzymatic etching).
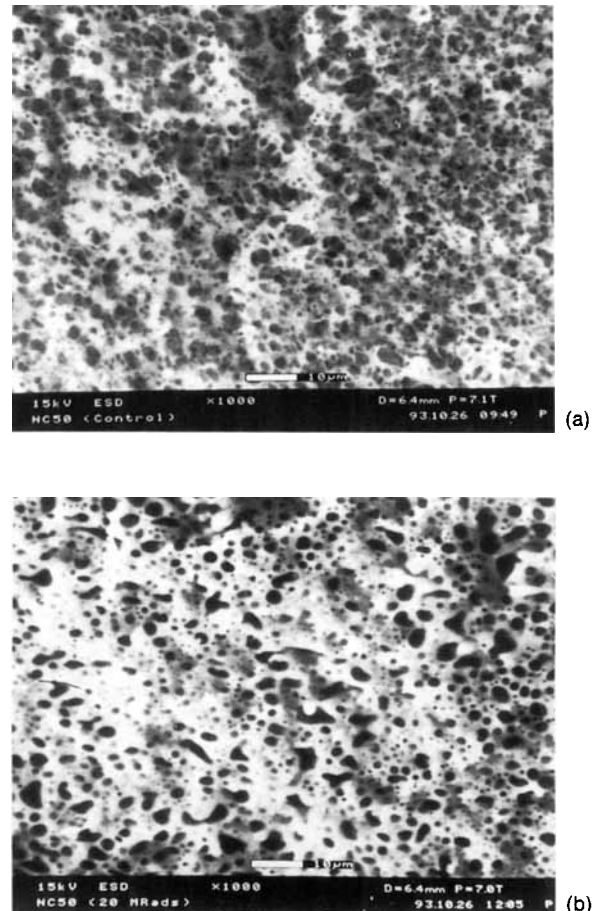
The WM 50 samples showed the most striking changes. The cross sections of the filaments prepared from the control pellets also show discrete (almost round or oblate) starch domains with a distribution of sizes (in the approximate range of 1-3 μm) dispersed in a matrix of the synthetic polymer

(Fig. 7). It can also seen that often thin webs of EVOH separate the starch domains. The structure of the filaments prepared from the irradiated pellets (200 kGys FIP) is distinctly different [Fig. 7(b,c)], whereby the starch domains are generally much larger in size (roughly 3–10 μm across) and go much deeper below the fracture surface. In fact, the morphology of the starch phase shows significant interconnectedness (more obvious in the higher magnification micrograph).

The cross sections of the control and the 200 kGys FIP NC 50 samples (Fig. 8) also show similarities to their WM 50 counterparts, though it can be seen that the irradiated native corn sample does not show as striking a change in the structure as the irradiated waxy maize sample. It should be mentioned here that for both the WM and NC cases, the morphology was not always uniform across the cross section of
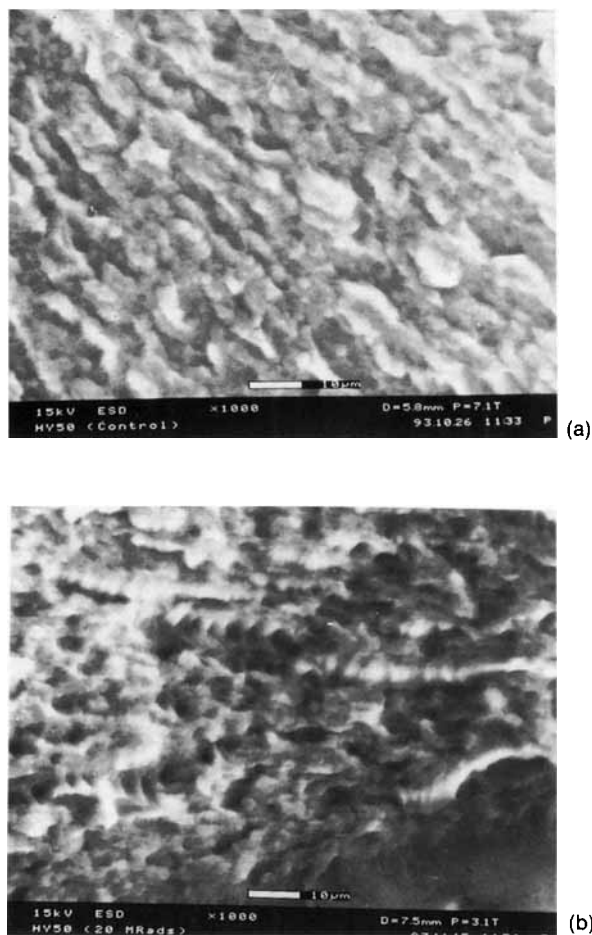

Figure 7   Micrographs of cross sections of WM 50 filaments, subsequent to enzymatic treatment to remove strach. The dark areas correspond to the regions where starch was etched out: (a) Control filament (1000X), (b) filament from 200 kGys irradiated pellets (FIP; 1000X), and (c) filament from 200 kGys irradiated pellets (FIP; 2000X).

Figure 8   Micrographs of cross sections of NC 50 filaments, subsequent to enzymatic treatment to remove starch. The dark areas correspond to the regions where starch was etched out: (a) Control filament (1000X) and (b) filament from 200 kGys irradiated pellets (FIP; 1000X).

(a)

(b)

Figure 9 Micrographs of cross sections of HY 50 filaments, subsequent to enzymatic treatment to remove starch: (a) Control filament (1000×) and (b) filament from 200 kGys irradiated pellets (FIP; 1000×).

the filaments; however, the micrographs shown are generally representative of the structures.

For the HY 50 samples, etching of the cross sections of these filaments did not seem to be very successful for reasons not completely understood; as can be seen, there are no clear domains of (etched out) starch (Fig. 9). Given the sizes of the starch molecules, it is difficult to imagine that phase separation does not occur between the starch and the EVOH. It is possible that the interactions between the linear amylose molecules and the EVOH prevent the formation of clear domains which can be attacked by the enzyme.

Obviously, the change in the structure of the NC and WM blends came about during the melt-reprocessing of the irradiated pellets through the capillary setup used to produce the filaments. As mentioned earlier, in our blends, the radiation has the effect of modifying starch to a much greater extent than the

synthetic polymer. Therefore, the differences observed between the control and irradiated blends can be attributed mostly to the differences in the starch present in the two blends. It can be imagined that the molecular scission in the starch macromolecules lowers their average molecular weight and increases their mobility in the blend, especially given the fact that the waxy maize and native corn starch used in the blending must have contained strong intermolecular forces (since complete dissolution of the precursor or extruded waxy maize and native corn starches was not possible even in good solvents such as alkali). It is also possible that some interfacial reactions might have occurred between the starch and EVOH phases during irradiation, but this hypothesis was not tested.

Other studies on blends of starch and synthetic polymers indicate that unmodified starch blended with thermoplastics maintains its granular shape despite the action of the shear forces during the processing.[4,7,12,19,46] This starch filler does not serve any reinforcing function, which is not surprising since there is no mechanism of stress transfer across the interface between the starch and the thermoplastic matrix. In such cases, the discrete starch domains (or fragmented granules) would tend to act almost as stress concentrators for the tensile stress fields. Consequently, in almost all cases, a decrease in the elongation to break and the ultimate tensile strength is seen as increasing amounts of starch are blended into a thermoplastic. Processing methods that allow an increased dispersion of starch generally have resulted in products with better properties. The dispersion of starch can be attained by gelatinization of the starch previous to the mixing[9] or through chemical modification such as derivatization of the starch hydroxyl groups to acetate or hydroxypropyl moieties.[20] Surface modification of starch granules to increase their hydrophobicity also results in marginal improvements in properties of starch blends with polyethylene.[19] It has also been shown that coprecipitation of starch xanthide and thermoplastics from solution[7] or casting of such blends from aqueous dispersions[8] leads to films with better mechanical properties than those made from dry milled blends. The improved mixing between the blend components was proposed as being responsible for this difference. Otey et al.[10] also showed that the dispersion of the starch can be made more effective not only through the traditional gelatinization using a combination of heat and moisture, but also through the use of urea and other polyols that allow the preparation of well-mixed blends through semi dry processing.

All this indicates that the dispersion of starch in its blends with other thermoplastics plays a crucial role in the eventual properties attainable by the blend. If the starch is blended with a thermoplastic such that it does not lose its granular structure, then the blend is likely to behave like a thermoplastic with nonreinforcing filler. If the starch granular structure is disrupted completely before or during blending, then the starch is likely to act more like a traditional polymer in that it is mobile at a molecular level during blending. It has also been mentioned[10] that interactions between starch and thermoplastic may prevent retrogradation of the starch and therefore allow the blend to retain desirable mechanical properties even upon aging. In our case, the irradiation of the granular native corn and waxy maize starches in their blends with EVOH should certainly allow for much better mobility of the starch and hence lead to a different microstructure for the blend.

The behavior of the high-amylose starch-containing blends, though very different from the native corn and waxy maize-containing blends, seems consistent across the various probes of structure and properties employed in this study. The thermal and mechanical property measurements and the morphology studies all seem to indicate that there might be some interactions between these high-amylose starch molecules and the EVOH, consistent with the rheological data presented elsewhere.[29] Such an interaction might underlie the increase in the viscosity of the irradiated HY blends, the lower levels of crystallinity obtained in the DSC, and the comparative insensitivity of the mechanical properties and the structure these blends to radiation. It should also be kept in mind that the precursor Hylon material was modified physically through a spray-drying process and hence certainly lacked the strong intermolecular forces most likely present in the (unirradiated) granular waxy maize and native corn starches used in this study.

Conclusions

Irradiation of starch by an (ionizing) electron beam results in significant physical modifications at the molecular level, of which the primary ones are the scission of bonds and disruption of intermolecular structures. This is evident from the shift to higher GPC elution volumes for the irradiated starches as compared to the control samples. In contrast, EVOH, the synthetic polymer that forms the second component of the blends used in this study seems

to be relatively unaffected by irradiation. In comparison to filaments prepared from control pellets, filaments prepared from irradiated blend pellets show some changes in their microstructure and an improvement in mechanical properties (stress-to-break and strain-to-break) for starch content less than 50%. Microstructural examination indicates that the starch-containing domains are bigger and somewhat interconnected for the latter samples; this is seen best in the waxy maize-containing smaple. This can be attributed to the greater mobility of the (fragmented) irradiated starch present in the blend.

Disruption of granular structure and/or macromolecular scission can also be effected by other treatments such as acid degradation or mechanical processing, but these are generally complex and time-consuming in comparison to irradiation, which does not require much preparation of the raw materials, is quick, and requires no subsequent purification. Consequently, irradiation-based physical modification of starch seems to offer a simple and straightforward method (that could be industrially viable) to effect desirable improvements in the properties of blends of starches with thermoplastic materials.

REFERENCES

1. *Facing America's Trash: What's Next for Municipal Solid Waste,* OTA-O-424, U.S. Govt. Printing Office, Washington, D.C., 1989.
2. R. W. Lenz, *Adv. Polym. Sci.,* **107,** 1 (1993).
3. G. Swift, *Acc. Chem. Res.,* **26,** 105 (1993).
4. G. J. L. Griffin, in *Fillers and Reinforcements for Plastics,* ACS Adv. Chem. Ser. **134,** American Chemical Society, Washington D.C., 1974, pp. 156–170.
5. G. J. L. Griffin, U.S. Pat. 4,016,117 (1977).
6. G. J. L. Griffin, U.S. Pat. 4,021,388 (1977).
7. R. P. Westhoff, F. H. Otey, C. L. Mehltretter, and C. R. Russell, *Ind. Eng. Chem. Prod. Res. Dev.,* **13,** 123 (1974).
8. F. H. Otey, R. P. Westhoff, and C. R. Russell, *Ind. Eng. Chem. Prod. Res. Dev.,* **16,** 305 (1977).
9. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Res.,* **19,** 592 (1980).
10. F. H. Otey, R. P. Westhoff, and W. M. Doane, *Ind. Eng. Chem. Prod. Res. Dev.,* **26,** 1659 (1987).
11. Y. Tokiwa, A. Iwamoto, and M. Koyama, *Polym. Mat. Sci. Eng.,* **63,** 742 (1990).
12. B. A. Ramsay, V. Langlade, P. J. Carreau, and J. A. Ramsay, *Appl. Environ. Microbiol.,* **59,** 1242 (1993).

13. I. Tomka, R. F. Stepto, and B. Dobler, Eur. Pat. Appl. 88810130.0 (1987).
14. I. Tomka, R. F. Stepto, and B. Dobler, Eur. Pat. Appl. 88810548.3 (1987).
15. F. H. Otey, A. M. Mark, C. L. Mehltretter, and C. R. Russell, *Ind. Eng. Chem. Prod. Res. Dev.,* **13,** 90 (1974).
16. B. T. Nwufo and G. J. L. Griffin, *J. Poly. Sci., Polym. Chem. Ed.,* **23,** 2023 (1985).
17. E. R. George, T. M. Sullivan, and E. H. Park, *Polym. Eng. Sci.,* **34,** 17 (1994).
18. S. Simmons, C. Weigand, R. Albalak, R. C. Armstrong, and E. L. Thomas, in *Fundamentals of Biodegradable Materials and Packaging,* D. Kaplan, C. Ching, and E. L. Thomas, Eds., Technomic, Lancaster, 1993, pp. 171–207.
19. R. L. Evangelista, Z. L. Nikolov, W. Sung, J.-L. Jane, and R. J. Gelina, *Ind. Eng. Chem. Res.,* **30,** 1841 (1991).
20. C. L. Swanson, R. P. Westhoff, and W. P. Doane, in *Proc. of the National Corn Utilization Conference II,* National Corn Growers Association, St. Louis, 1988.
21. S. Simmons and E. L. Thomas, *Polymer,* to appear.
22. M. A. Villar, E. L. Thomas, and R. C. Armstrong, *Polymer,* to appear.
23. L.-P. Yu and J. E. Rollings, *J. Appl. Polym. Sci.,* **33,** 1909 (1987).
24. *Standard Test Method for Tensile Properties of Single Textile Fibers* (ASTM D 3822-91) (1991).
25. A. Charlesby, in *Irradiation Effects on Polymers,* D. W. Clegg and A. W. Collyer, Eds., Elsevier, London, 1991, pp. 39–78.
26. Y. Hama and T. Hirade, *Radiat. Phys. Chem.,* **37,** 59 (1991).
27. D. J. Carlsson, S. Chmela, and D. M. Wiles, *Polym. Deg. Stab.,* **31,** 255 (1991).
28. K. B. Ekman and J. H. Nasman, *J. Appl. Polym. Sci.,* **50,** 233 (1993).
29. A. D. Sagar, M. A. Villar, R. C. Armstrong, E. L. Thomas, and E. W. Merrill, *J. Appl. Polym. Sci.,* **61,** 157 (1996).
30. R. L. Whistler and T. R. Ingle, in *Starch: Chemistry and Technology,* 1st ed., R. L. Whistler and E. F. Paschall, Eds., Academic Press, New York, 1965.
31. J. Pruzinec and O. Hola, *J. Radioanal. Nucl. Chem.-Lett.,* **118,** 427 (1987).
32. J. Trzebinski and L. Ehrenberg, *Acta Chem. Scand.,* **13,** 1075 (1959).
33. L. Ehrenberg, M. Jaarma, and E. C. Zimmer, *Acta Chem. Scand.,* **11,** 950 (1957).
34. P. Colonna, A. Buelon, and C. Mercier, in *Starch: Properties and Potential, Crit. Rep. Appl. Chem.,* **13,** T. Galliard, Ed., Wiley, Chichester, 1987, pp. 79–114.
35. A. Hebeish, A. M. El-Naggar, F. El-Sisi, S. Abdel-Hafiz, and K. El-Salmwi, *Polym. Deg. Stab.,* **36,** 249 (1992).
36. A. H. Young, in *Starch: Chemistry and Technology,* 2nd ed., R. L. Whistler, J. N. BeMiller, and E. F. Paschall, Eds., Academic Press, Orlando, 1984, pp. 249–283.
37. B. J. Bauer, L. J. Fetters, W. W. Graessley, N. Hadjichristidis, and G. F. Quack, *Macromolecules,* **22,** 2337 (1989).
38. J. Roovers, L.-L. Zhou, P. M. Toporowski, M. van der Zwan, H. Iatrou, and N. Hadjichristidis, *Macromolecules,* **26,** 4324 (1993).
39. G. Giezlenz and B.-J. Jungnickel, *Colloid Polym. Sci.,* **260,** 742 (1982).
40. F. J. Zoepfl, V. Markovic, and J. Silverman, *J. Polym. Sci. Polym. Chem. Ed.,* **22,** 2017 (1984).
41. A. L. Blackwell, in *High Performance Polymers: Their Origin and Development,* R. B. Seymour and G. S. Kirshenbaum, Eds., Elsevier, New York, 1986. pp. 425–435.
42. P. Harnischfeger, P. Kinzel, and B. -J. Jungnickel, *Angew. Makromol. Chemie,* **175,** 157 (1990).
43. S. Thomas, B. R. Gupta, and S. K. De, *Polym. Deg. Stab.,* **18,** 189 (1987).
44. L. Minkova and M. Nikolova, *Polym. Deg. Stab.,* **23,** 217 (1989).
45. A. Huang, pers. commun., Jan. 13, 1993.
46. J. S. Penansky, J. M. Long, and R. P. Wool, *J. Polym. Sci., Polym. Phys. Ed.,* **29,** 565 (1991).